MASTER COPY KEEP THIS COPY FOR REPRODUCTION PURPOSES

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
17 October 1995

3. REPORT TYPE AND DATES COVERED
Final Report (8 July 92-30 June 95

4. TITLE AND SUBTITLE
Anionic Lewis Acids: A Chemical Oxymoron

5. FUNDING NUMBERS
DAAL03-92-C-0038

6. AUTHOR(S)
Larry A. Dominey, Richard Laura, Wayne J. Clark, Tom J. Blakley, Warren Averill, and Jun-Rui Yang

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Covalent Associates, Inc.
10 State Street
Woburn, MA 01801

8. PERFORMING ORGANIZATION REPORT NUMBER
C-109

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

An emerging class of unusual compounds "Anionic Lewis Acids" was the center of study in this research program. We carried out *ab initio* molecular orbital calculations on two of these anions, $(CF_3SO_2)_2N^-$, and $(CF_3SO_2)_3C^-$. A multi-nuclear FT-NMR study was conducted on a series of anions and the results could be rationalized on the number of substituents present in the anions. In addition, a new anionic Lewis acid was synthesized and evaluated.

14. SUBJECT TERMS
anionic lewis acid, ab initio, synthesis, methide, FT NMR, imide, multi-nuclear

15. NUMBER OF PAGES
12

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

Anionic Lewis Acids: A Chemical Oxymoron

Final Report

Larry A. Dominey, Richard Laura, Wayne J. Clark, Tom J. Blakley, Warren Averill, and Jun-Rui Yang

October 17, 1995

U.S. Army Research Office

Grant DAAL03-92-C-0038

Covalent Associates, Inc.

10 State Street

Woburn, MA 01801

Approved for public release; distribution unlimited.

Table of Contents

Anionic Lewis Acids: A Chemical Oxymoron

INTRODUCTION

Strong acids and their salts are important in three technological areas; for example, the acids are used as catalysts in epoxy and siloxy polymerization processes for thin film coatings. Salts of their conjugate bases serve as supporting electrolytes in high energy density batteries and advanced fuel cells. These technologies would benefit from the introduction of new, improved anions which are stable conjugate bases derived from powerful acids. Such anions need to be chemically robust, thermally stable, non-toxic, environmentally safe, and cost-effective.

One of our current areas of interest involves the synthesis and evaluation of novel lithium salts for use in primary and secondary (rechargeable) lithium batteries. In the course of our work, we recently prepared two novel anions which share a unique and unexpected property: they appear to interact strongly with weak electron sources such as xenon. This unusual behavior results from the asymmetric distribution of charge within the molecular structure of the anion. These molecular anions possess regions which are actually very electron-deficient and this high degree of charge asymmetry leads to a variety of novel and useful properties. These compounds, in addition to their commercial potential, encourage the testing of theoretical, mechanistic, and structural hypotheses.

We have named this emerging class of unusual compounds "Anionic Lewis Acids", an apparent contradiction in terms made possible by their unique molecular complexity. Hence the term "chemical oxymoron".

In this research program, we proposed to conduct a multi-nuclear FT-NMR spectroscopy study on three of these anions with the goal of developing a predictive knowledge base that can be used to guide the synthesis of new locally electron-deficient anions. Additionally, we proposed to carry out *ab initio* molecular orbital calculations on two of the best characterized of these anions, $^{-}N(SO_2CF_3)_2$ and $^{-}C(SO_2CF_3)_3$, and to compare the NMR data with the molecular orbital calculations of electron density distribution. Finally, we proposed to synthesize and characterize representative compounds from two new families of potential anionic Lewis acids.

BACKGROUND

A persistent goal of lithium battery electrolyte research has been the development of improved counterions of Li^+ which are concurrently non-toxic, thermally and chemically stable, and, in the case of rechargeable cells, cycle well against the lithium anode. Triflate ($CF_3SO_3^-$) fulfills these criteria, but unfortunately exhibits relatively poor conductivity in a variety of non-aqueous solvents used in batteries.

Several years ago we set out to develop anions which retained triflate's excellent stability but were much more conductive. Based on our appreciation that the CF_3SO_2 group is the most electron-withdrawing functional group known, we sought to "double" and "triple" its activity by bonding it to nitrogen and carbon core atoms. Thus, the following homologous series of anions can be written

$$(CF_3SO_2)O^- \;<\; (CF_3SO_2)_2N^- \;<\; (CF_3SO_2)_3C^-$$

triflate imide methide

wherein the negative charge is more extensively delocalized on going from oxygen to nitrogen to carbon. Greater delocalization of negative charge will result in the formation of fewer ion pairs in solution and higher solution conductivity.

As part of this research program, we recently synthesized lithium bis(trifluoromethylsulfonyl)imide, $(CF_3SO_2)_2N^-Li^+$, and lithium tris(trifluoromethylsulfonyl)methide, $(CF_3SO_2)_3C^-Li^+$, which we refer to familiarly as lithium imide and lithium methide. These compounds dissolve readily in solvents, such as tetrahydrofuran, commonly used in non-aqueous battery studies, giving solutions with extremely high ionic conductivity. As anticipated, the methide was more conductive than the imide. These salts possess low crystal lattice energies and weak coulombic interactions. The physical manifestations of these attributes are that these ionic compounds show high solubilities and enhanced tendency toward dissociation into free ions, even in weakly solvating solvents such as diethyl ether. This is a striking phenomenon when compared to the behavior of most carbanions and anionic imides. Furthermore, both salts demonstrated excellent stability when subjected to tests typically required of liquid lithium battery electrolytes.

In the course of characterizing these two new anions, we realized that we had apparently discovered a new, or at least essentially unrecognized, class of chemical compounds: negatively charged Lewis acids. There are two lines of experimental evidence in support of this idea.

First, the ability of the imide anion to form a bis adduct with xenon was demonstrated by DesMarteau and coworkers (1) and the existence of the xenon-nitrogen bond was confirmed by X-ray crystallography by Schrobilgen (2). The ability of the imide to form a N-Xe bond suggests substantial electropositive character on the nitrogen. Recently, Seppelt (3) was not successful in forming an analogous xenon-methide adduct.

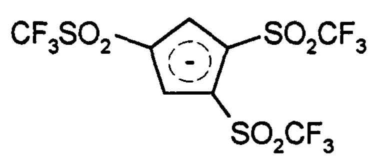
We suspect his failure may have been due to steric factors rather than lack of intrinsic Lewis acidity.

Second, we determined the ^{13}C NMR spectrum of the methide anion and observed two resonances, at 123.27 and 119.08 ppm relative to TMS. Both the central and trifluoromethyl carbons of this carbanion are strongly deshielded, whereas carbanionic carbons typically exhibit weak downfield shifts. Indeed, the central carbon of the methide anion shows the greatest downfield shift of any carbanion ever prepared. The central carbon atom is deshielded to a degree comparable to the CF_3 group carbon atom and the chemical shift of the central carbon's resonance is more suggestive of a carbocation. We suspected that the negative charge of the methide anion resides in the O=S=O and fluorine orbitals of the molecule, particularly spread out over the oxygens. The multi-nuclear NMR study was proposed to resolve this issue.

RESEARCH PROGRAM OBJECTIVES

As originally proposed, this research program had two main objectives. The first objective was to characterize the electron distribution in highly asymmetric charge distributed anions by conducting a high-field multi-nuclear FT-NMR spectroscopy study of some recently prepared anionic Lewis acids. In parallel with the NMR work, *ab initio* molecular orbital calculations on the imide and methide anions were proposed. The relative electron densities on carbon, fluorine, nitrogen, oxygen, and sulfur atoms (ions) in CF_3SO_3Li, $(CF_3SO_2)_2NLi$, and $(CF_3SO_2)_3CLi$ determined by NMR were to be compared with the molecular orbital calculations of electron density distribution.

The second objective involved a synthetic effort directed toward the preparation of new compounds representative of novel classes of anionic Lewis acids. The specific compounds proposed as synthetic targets were tris(trifluoroacetyl)methide, $(CF_3CO)_3C^-$, and tris(trifluoromethylsulfonyl)cyclopentadienylide, $(CF_3SO_2)_3Cp^-$.



As part of the characterization of the new anions, we intended to determine their electrochemical stability windows in common lithium battery electrolytes and to test their chemical stability toward lithium, and to compare these results with those obtained with lithium imide and lithium methide.

SUMMARY OF IMPORTANT RESULTS

Molecular Orbital Calculation

The *ab initio* molecular orbital calculations on the methide and imide anions were performed by Professor Mary Jo Ondrechen in the Chemistry Department at Northeastern University using the Hartree-Fock-Slater Discrete Variational Method (HFS-DVM). The basis set includes the 1s-2s and 2p functions on all C, Oand F atoms; the 1s-3s and 2p-3p functions on the N atom of imide; the 1s-3s, 2p-3p and 3d functions on the S atom. The calculation on the methide anion was based on the atomic coordinates published by Seppelt (3). Table 1 summarizes the calculated Mulliken populations for each atom in the

Table 1: Mulliken charges of atoms in $^{-}C(SO_2CF_3)_3$

Atom	Orbital	Electrons	Net Charge on Atoms
S	3s	1.25	
	3p	2.79	+0.89
	3d	1.07	
C_{distal}	2s	0.90	+0.84
	2p	2.26	
F	2s	0.90	-0.27
	2p	2.26	
O	2s	1.87	-0.48
	2p	4.61	
$C_{central}$	2s	1.24	-0.90
	2p	3.66	

methide anion, $^{-}C(SO_2CF_3)_3$. The sum over all these charges, each multiplied by the number of each atom in the anion , is -1.0, the charge of the anion.

From the data in Table 1, it can be seen that the trifluoromethyl group carbons and the sulfur atoms are the most electron deficient species in the anion (+0.84 and +0.89 e^-, respectively), with the central carbon (-0.90 e^-) exhibiting some electron deficiency relative to a formal charge of -1.0. The bulky SO_2CF_3 groups shield the negatively charged central carbon from the positive counterion, reducing the coulombic attraction and enabling the positive counterion (Li^+) to move freely. In addition, the separation between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in the methide anion is unusually large, 5.25 eV.

Molecular orbital calculations for the imide anion were based on a crystal structure of $NaN(SO_2CF_3)_2$ solvate containing one equivalent each of coordinated methanol and water. This crystal structure was determined by Professor Darryl DesMarteau at Clemson University and we thank him for providing us with the structure prior to publication.

Table 2 compares previously published HOMO energies for the triflate as well as imide and methide anions. Kita used a semi-empirical MNDO method (4) and Sanchez assumed interatomic bond lengths in his work (5). Our approach used an *ab initio* method together with crystallographic data for the bond lengths of the particular anions of interest, and therefore, we believe our data to be the most accurate. Nonetheless, the trend for triflate, imide and methide is consistent across the three groups of data. To our knowledge, methide has both the highest reported HOMO energy and the highest experimentally determined oxidation potential of any organic anion.

Table 2. Calculated HOMO Energies

Anion	Kita[22]	Sanchez[31]	this work
PF_6^-	--	--	-9.0
AsF_6^-	--	--	-9.2
triflate	-6.96	-7.48	--
imide	-8.19	-8.52	-9.5
methide	-8.70	--	-9.8

Multi-nuclear NMR Spectroscopy

The multi-nuclear FT-NMR investigations of lithium triflate, $CF_3SO_3^-Li^+$, lithium imide, $(CF_3SO_2)_2N^-Li^+$, and lithium methide, $(CF_3SO_2)_3C^-Li^+$, were carried out by Dr. Shaoxiong Wu at Emory University. The ^{15}N NMR spectrum of the imide, obtained in acetone-d_6 at 500 MHz, consisted of a singlet at 239.5 ppm relative to CD_3CN as internal reference. The NMR results comfirms that the nitrogen atom is one of the most electron deficient species in the molecule

The ^{17}O NMR spectra of the three anions were determined at 500 MHz in CD_3CN solvent containing D_2O as internal reference. All the resonance signals observed were singlets, leading us to conclude that the oxygen atoms in each compound are magnetically and structurally equivalent on the NMR time scale. The chemical shifts of the ^{17}O signals were: triflate, 166.4 ppm; imide, 166.5 ppm; and methide, 169.3 ppm.

The difference in ^{17}O chemical shifts is not very large. However, the relative deshielding of the oxygens of the methide anion implies less electron density on its individual oxygen atoms. In fact, this trend could be rationalized for all three anions. As the number of oxygens increases, the lower amount of negative charge per oxygen is reflected in the NMR shift data.

Synthesis of Cyclopentadienylide

Sodium cyclopentadienylide (NaCp, 0.20 mol; 100 ml of a 2M solution in THF obtained from Aldrich) and sodium hydride (17.7g of 95% NaH from Aldrich; 0.70 mol; 3.5 equiv.) were mixed with ~300ml of additional anhydrous THF in the Parr bomb liner in a glovebox. Final concentration of NaCp is ~ 0.5M. The covered liner was removed from the drybox and the Parr bomb was assembled as quickly as possible, minimizing exposure of the reaction mixture to air. The bomb was cooled in a dry ice/isopropanol bath until the internal temperature as measured with a low temp thermometer inserted in the bomb's thermowell was ~ -50°C. Trifluoromethylsulfonyl fluoride, aka PMSF for "perfluoromethylsulfonyl fluoride", obtained *gratis* from 3M Company, was condensed into the bomb using the customary vacuum line + polyethylene bag technique. The amount of PMSF introduced into the bomb was estimated reasonably accurately by assuming that a 4 liter bag holds 30g of gas; the actual weight of PMSF used was determined from the cylinder weight. In a typical experiment, three bags of PMSF (93g; 0.61 mol; ~3 equiv.) were condensed. The reaction mixture was then stirred and heated at ~75°C for ~40 hours. After cooling and venting the bomb, the reaction mixture was *slowly and cautiously* added to a liter of stirred ice water: there is plenty of unreacted NaH in the mixture & the reaction with water is quite lively. The strongly basic aqueous mixture was neutralized with 6M HCl until the pH was ~7 as determined with pH paper. This neutralization step prior to extraction completely eliminated the formation of intractable

emulsions that occurred when the basic reaction mixture was extracted with organic solvents. Any trifluoromethylsulfonyl-substituted cyclopentadienes of interest will remain completely ionized at pH 7. The neutral aqueous solution was extracted with several portions of ethyl acetate, the combined organic extracts were washed with saturated aqueous NaCl , dried with $MgSO_4$, filtered, and the filtrate was concentrated on a rotary evaporator. After being kept under vacuum at room temperature for several hours, the residue amounted to 35g of a dark red, foamy semi-solid.

This crude product was dissolved in hexane/EtOAc (3:2, v:v) and applied to a column of silica gel (500g of silica, 70-230 mesh, forming a column 7.5 cm in diameter & 23 cm in height). The column was eluted with increasing concentrations of ethyl acetate in hexane, taking large fractions by visual observation of the dark red bands moving down the column. The first couple of fractions, eluted with 40-60% EtOAc in hexane, amounted to ~12g of dark red syrup. This material is junk - no aromatic protons detected by NMR. The next fraction, eluted with 100% ethyl acetate, afforded ~13g of dark red solid after evaporation & drying under vacuum. This fraction, analyzed by 300MHz ^{1}H NMR, contained the desired product(s): sodium 1,3-bis(trifluoromethylsulfonyl)-cyclopentadienylide, mainly, as well as any 1,2-disubstituted & 1,2,4-trisubstituted compounds. Further elution of the silica column, adding 5-10% ethanol to the ethyl acetate, gave only 0.5g of dark red gum. By weight, the recovery was ~75% of the material applied to the column.

The dried EtOAc extract was dissolved in water (very soluble) and suction filtered through a Whatman GF/F glass fiber filter to remove some fine particulates. The filtrate was mixed with a similarly filtered aqueous solution of tetraethylammonium chloride. Approximately two equivalents of $Et_4N^+Cl^-$ were used, basing the calculation on the assumption that the EtOAc eluate is composed entirely of sodium 1,3-bis(trifluoromethyl-sulfonyl)cyclopentadienylide. A precipitate formed immediately upon mixing the two aqueous solutions. The mixture was stirred overnight at room temperature, the precipitate was collected by suction filtration, washed with water, and dried under vacuum at 40°C. The product, obtained in 65% yield based on the aforementioned assumption, was tetraethylammonium 1,3-bis(trifluoromethylsulfonyl)cyclopentadienylide, a pink powder, mp 84-86°C. Using this method, attempts to obtain tetraethylammonium salts from the materials in the other eluates from the silica column were completely unsuccessful. Attempts to isolate and purify significant quantities of the other Et_4N^+ cyclopentadienylide isomer(s) presumably present in the aqueous filtrate from the Et_4N^+ 1,3-bis(Tf)Cp were equally unproductive. From the 13g of dried EtOAc eluate we obtained 11g (12%) of reasonably pure teraethylammonium salt ($C_{15}H_{23}F_6NO_4S_2$: 459.51 g/mol) based on sodium cyclopentadienylide starting material.

For further purification, the tetraethylammonium salt was dissolved in methylene chloride (very soluble) and applied to a column of silica gel (using about 20g of silica per gram of salt) in methylene chloride. The column was washed thoroughly with methylene chloride - nothing moves. The pure salt was then eluted with 3% methanol (by volume) in methylene chloride and the product was collected by visually monitoring the column. The

purified compound was obtained as a dark red powder, mp 86-88°C; by weight, 85% of the material applied to the column was recovered. Alternatively, the salt could be recrystallized from diisopropyl ether + hexane to give pale pink crystals, mp 87-88°C. The only advantages to recrystallization were that a definitely crystalline, less colored product was obtained instead of the dark red powder from the column. Recrystallization was more time-consuming in achieving the proper solvent mixture, as well as less satisfactory in regard to material recovery. The final products from each process were identical spectroscopically (IR & NMR); indeed, there is no spectrally apparent change effected by purification - only the slight improvement in melting point. Recrystallized tetraethylammonium 1,3-bis(trifluoromethylsulfonyl)cyclopentadienylide was submitted for elemental analysis:

Calculated for $C_{15}H_{23}F_6NO_4S_2$: C, 39.20; H, 5.06; N, 3.05; S, 13.95 %
Found: C, 39.47; H, 5.11; N, 3.00; S, 13.87 %

We attempted to prepare the lithium salt of 1,3-bis(trifluoromethylsulfonyl) cyclopentadienylide by the metathesis reaction between the tetraethylammonium salt and LiBr in THF. The cyclopentadienylide salts (Li^+, Na^+, or Et_4N^+) are soluble in THF, as is lithium bromide; however, tetraethylammonium bromide is insoluble. Therefore, THF solutions of LiBr & tetraethylammonium cyclopentadienylide were prepared and suction filtered to remove any particulate contaminants. The solutions were mixed and magnetically stirred overnight (~20 hours) at ambient temperature. A precipitate formed as soon as the solutions were mixed. After stirring overnight, the supernatant liquid appeared distinctly lighter in color than it had initially, changing from a reddish-pink at the start of the reaction to yellowish. The reaction mixture was filtered by suction through a Whatman GF/F glass fiber filter to separate the precipitated tetraethylammonium bromide. The filtrate was concentrated on a rotary evaporator & the residual syrup was dissolved in diethyl ether. The ethereal solution was washed with several portions of water to remove excess LiBr. From this point, there were slight variations in the procedure. At first, the ethereal solution was treated like any other organic extract: it was washed with saturated aqueous NaCl & dried with $MgSO_4$, filtered, concentrated to dryness by rotary evaporation, & finally kept under vacuum to remove residual solvent. This method began to look problematical when the ether solution containing drying agent ($MgSO_4$) darkened on standing. Elimination of the drying agent made no difference. Thinking that the lithium salt was intolerant of contact with other cations,we washed the ethereal solution only with deionized water, concentrated it on a rotary evaporator & popped the flask into the vac oven as quickly as possible. In other words, all operations after the suction filtration of the THF reaction mixture through GF/F were carried out without interruption & as rapidly as possible. All to no avail. If we worked fast enough to avoid significant darkening of the ether solution, the residue left after removal of the ether gradually turned black, even under vacuum. Keeping the residue under vacuum at room temperature or higher (up to 70°C.) made no apparent difference - the material turned black regardless of temperature. Thorough drying under vacuum at 70°C afforded a glassy, crystalline black product of indeterminable melting point: it seemed to melt (or decompose?) over a broad range, but the endpoint could not be seen. Attempts to purify the black solid by chromatography or

recrystallization were futile, usually resulting in black syrups or gums that didn't have the decency to solidify.

From the infrared spectra, it appears that the trifluoromethylsulfonyl groups are still intact in the black solid: for the tetraethylammonium salt, 1335 & 1117 cm^{-1} are the asymmetric & symmetric SO_2 stretch; broad, intense band ~1200 cm^{-1} is C-F stretching. The black solid has SO_2 stretching at 1340 & 1124 cm^{-1}; C-F stretching at 1201 cm^{-1}. The spectral overlay shows differences in the 1500-1375 cm^{-1} & 1075-700 cm^{-1} regions, but that could all be due to the change in cation. Perhaps the lithium salt is in there, but we ran out of time to purify it.

Evaluation of Tetraethylammonium 1,3-Bis(trifluoromethylsulfonyl)cyclopentadienylide

The conductivity of the title compound was measured using acetonitrile as a solvent. Molar concentrations of the salt were increased until the conductivity was maximized. The maximum was found at a concentration of 1M (4.60g/10mL acetonitrile), where the conductivity of the solution was measured to be 32.5 milliSiemens.

Cyclic voltametry experiments were conducted in order to determine the anodic and cathodic limits of the salt. A three electrode system was used: glassy carbon ($A=0.07cm^2$) as the working electrode; platinum as the counter electrode; and silver wire as the reference electrode. A 1M solution in acetonitrile was used as the electrolyte. Its open circuit potential was +150mV. The anodic limit (X^- to $X+e^-$) is 1.29 V *vs.* Ag. The cathodic limit (Y^++e^- to Y) is -2.12 V *vs.* Ag.

Attempted Synthesis of Tris(trifluoroacetyl)methide

We carried out four separate experiments attempting to synthesize tris(trifluoroacetyl)methane and/or its lithium salt. In the first reaction, We essentially followed the scheme in the proposal and used butyl lithium as the base. The attempted "double deprotonation" was done outside the dry box, both to avoid filling the box with butane and so that the reaction flask could be cooled in ice during the exothermic reaction. Hexafluoroacetylacetone (14 ml; 20.6 g; 0.1 mol) was dissolved in dry THF (~250 ml) in a dry one-liter round bottom flask containing a stir bar and equipped with a pressure-equalizing addition funnel and argon inlet. The flask was cooled in an ice bath and a solution of *n*-butyl lithium in hexane (100 ml of a 2.5M solution; 0.25 mol) was added from the funnel over ~30 minutes. Gas evolution was observed. After the addition, the flask was allowed to warm to room temperature, when it was securely stoppered and sent into the glove box. The flask contents were transferred to the liner of the Parr bomb inside the box, then the liner was removed and the bomb was assembled. The bomb was cooled in dry ice & then trifluoroacetyl chloride (one four-liter bag = 26.5 g; 0.2 mol) was condensed into the bomb in the usual manner. We decided to use trifluoroacetyl chloride instead of fluoride largely because it is an order of magnitude less expensive, it is a bit less volatile, and it is more readily available. The bomb was heated at 70° C for two days, cooled and the reaction mixture worked up by quenching in water and extracting with

EtOAc. The extracts were dried and concentrated; the crude product (54 g of acrid, dark brown liquid) was vacuum-transferred to give 42 g of pale yellow liquid. This material was fractionally distilled to give, essentially, trifluoroacetic acid and about 14 g of high-boiling liquid, bp 33-34° under vacuum; bath temp ~ 65-70° C. Analysis by IR shows significant aliphatic C-H stretch (2967, 2939, 2879 cm^{-1}), C=O stretch (1774 cm^{-1}), not a trace of O-H stretching. The result ws somewhat disappointing, since any diketone or triketone products that one might imagine coming out of this reaction would be substantially enolized & should exhibit O-H stretching in their protonated form. Without having done any further work on this compound, We think that the first equivalent of base abstracted a proton, as expected, to give an enolate which then reacted with the second equivalent of *n*-BuLi by 1,2 addition to the non-enolized carbonyl giving a tertiary alkoxide. Then reaction with trifluoroacetyl chloride resulted in acylation of the oxygens to give an enol trifluoroacetate plus the trifluoroacetyl ester of the tertiary alcohol.

In another experiment, the thallium salt of hexafluoroacetylacetone was allowed to react with excess (~5 equivalents) trifluoroacetyl chloride in diethyl ether solvent at temp. from -78° C to ambient, but workup gave only starting material.

Experiment #3 involved reaction of hexafluoroacetylacetone (14 ml; 20.6 g; 0.1 mol) with NaH (6 g: 0.25 mol) in diethyl ether in a 500 ml 3-neck roundbottom flask equipped with a stir bar and cold finger condenser containing dry ice. The reaction flask was then cooled in liquid nitrogen until the reaction mixture was almost frozen, the flask was evacuated & trifluoroacetyl chloride (~4 liters; 25 g; 0.19 mol) was condensed into the system using the customary polyethylene-bag technique. The reaction mixture was allowed to warm to ambient temperature as slowly as possible, with the outlet of the dry ice condenser remaining connected to the 4 liter bag used to introduce the gas; in this way, one can keep the gaseous reactant in the system, even if its vaporization cannot be prevented. Workup by aqueous quench, extraction, and fractional distillation gave diethyl ether, trifluoroacetic acid, and 6.3 g of glistening white crystals which solidified in the condenser. The crystals were extremely soluble in ether but insoluble in methylene chloride and melted at 93-95° C in a sealed capillary; melting was accompanied by vigorous bubbling, almost as if solvent was boiling out of the crystals.

The same product was obtained in better yield from the final reaction. In a glove box, dry NaH (6 g; 0.25 mol) was mixed with dry THF (~200 ml) in a dry 500 ml roundbottom flask containing a stir bar. The flask was sealed with a septum, removed from the box, & cooled in ice. Hexafluoroacetylacetone (14 ml; 20.6 g; 0.1 mol) was added to the flask from a syringe over about 30 minutes - lots of gas evolved. After complete addition, the ice bath was removed & the mixture was stirred under an argon purge while warming to room temp. The flask was returned to the glove box, where the contents were transferred to the Parr bomb liner. The bomb was assembled in the usual way, chilled, and trifluoroacetyl chloride (~4 liters; 24.5 g; 0.19 mol) condensed in. The bomb was stirred at ambient temperature overnight, then heated to 70-75° C for ~20 hours; pressure = 100 psig. Workup by aqueous quench & ether extraction afforded ~38 g of soft solid. Purification by sublimation *in vacuo* afford three "crops" of product, all

identical in their infrared spectra: crop #1 amounted to 6.0 g of white powdery crystals, mp 109-110° C (sealed tube); crop #2, 3.8 g of pale pink powdery crystals, mp 93-95° C (sealed tube); and crop #3, 5.8 g of larger pale pink crystals, mp 109-110° C (sealed tube). These are samples 79-162-1,2,or 3, respectively. The IR spectra of these samples all contain prominent O-H stretch. No C=O stretch is present.

^{1}H and ^{13}C NMR on sample 79-162-1 dissolved in acetone-d_6 indicates there are four types of hydrogen, and there is no C=O carbon. However, we found later that the sample was changing in acetone overnight. Therefore an elaborate NMR study on sample 79-162-1was carried out by Dr. Shaoxiong Wu at Emory University. The sample was dissolved in THF-d_8. Its ^{1}H and ^{13}C NMR spectra were recorded as a function of time. Unlike in acetone-d_6, no obvious change in NMR spectra was observed in THF-d_8 solvent after a period of two weeks. Knowing the compound was stable in THF-d_8, a series of ^{13}C spectra were recorded with specific hydrogen decoupling to establish the C-H connectivity and to identify the neighboring groups. Combining all the spectral data, we came to the conclusion that sample 79-162-1 is the hydrate of hexafluoroacetone $(CF_3C(OH)_2)_2CH_2$, not the expected tris(trifluoroacetyl)methane. This is further confirmed by a mixed melting point and IR spectra comparison with a commercial sample.

LIST OF PUBLICATIONS

V. R. Koch, L. A. Dominey, C. Nanjundiah and M. J. Ondrechen, " The Intrinsic anodic Stability of Several Anions Comprising Solvent-Free Ionic Liquids", *J. Electrochem. Soc., submitted.*

LIST OF SCIENTIFIC PERSONNEL

Larry A. Dominey, Richard Laura, Wayne J. Clark, Tom J. Blakley, Warren Averill and Jun-Rui Yang.

No degree was awarded.

REFERENCES

1. J. Foropoulos and D.D. DesMarteau, *J. Am. Chem. Soc.*, **104**, 4260 (1982).

2. R. Dagani, review article in *Chemical and Engineering News*, p. 16, April 4, 1988.

3. L. Turowsky and K. Seppelt, *Inorg. Chem.* **27**, 2135 (1988).

4. F. Kita, A. Kawakami, T. Sonoda, and H. Kobayashi, in *New Sealed Rechargeable Batteries and Supercapacitors*, B.M. Barnett, E. Dowgiallo, G. Halpert, Y. Matsuda, and Z-i. Takehara, Editors, pp. 321, vol. 332, The Electrochemical Society, Pennington, NJ, (1993).

5. D. Benrabah, R. Arnaud, and J-Y. Sanchez, Fourth Int. Symp. on Polymer Electrolytes, Newport, RI, June 19-24, 1994.